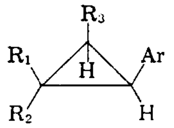
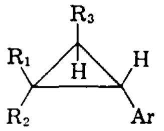
stituent are located on the same side of the ring (subsequently referred to as the *cis* configuration).

Chemical shifts of the alkyl proton resonances of adducts VII (both methylene and methyl protons) and VIII and of two methyl groups of adducts IX are 0.18 to 0.45 p.p.m. higher in the predominant isomers than the corresponding resonances of the minor adducts. Deriving geometrical parameters from scale models, it can be shown that the *cis* oriented alkyl groups are located in the diamagnetic shielding cone of the aryl ring[4] in or near those conformations of the aryl substituent which can be expected to be the most stable. In contrast the *trans* alkyl substituents find themselves in the paramagnetic zone in any conformation. Similarly, the observed larger shielding of the benzylic ring protons of the minor adducts are in line with expectations considering the diamagnetic effect of the *cis* oriented ring alkyl carbon carbon bonds.[5] Further support for this assignment is found in the larger spin-spin couplings of the vicinal ring protons with the benzylic protons in the predominant isomers. The stronger coupling has been demonstrated to be associated with *cis* orientation in a number of cyclopropanes with known configurations.[6] Finally, independent syntheses of the minor adducts to IV from *trans*-1-aryl-1-butenes *via* the stereospecific Simmons-Smith reaction[7] render the assignments of configurations unambiguous.

$X{-}C_6H_4{-}CHBr_2$

I, $X = H$, II, $X = CH_3$, III, $X = Cl$





VIIa, $R_1 = C_2H_5$, $R_2 = R_3 = H$
VIIIa, $R_1 = R_3 = CH_3$, $R_2 = H$
IXa, $R_1 = R_2 = R_3 = CH_3$
VIIb, $R_1 = C_2H_5$, $R_2 = R_3 = H$
VIIIb, $R_1 = R_3 = CH_3$, $R_2 = H$
IXb, $R_1 = R_2 = R_3 = CH_3$

ISOMER RATIOS AS OBTAINED FROM BENZAL BROMIDES[a] AND PHOTOLYSIS OF ARYLDIAZOMETHANES (IN PARENTHESES) WITH OLEFINS IV, V AND VI[b]

	Ar = C_6H_5	Ar = p-CH_3-C_6H_4	Ar = p-Cl-C_6H_4
VIIa/VIIb	2.1 (1.0)	2.8 (1.3)	2.1 (1.1)
VIIIa/VIIIb	2.4 (1.1)	4.5 (1.4)	3.4 (1.2)
IXa/IXb	1.3 (1.1)	1.4 (1.3)	1.4 (1.1)

[a] *n*-Pentane used as solvent. [b] Reaction temperature in both series, −10°.

The above mentioned correlations of relative magnitudes of vicinal proton spin spin coupling and of chemical shifts of ring protons with configurations[8] on three membered rings made it very probable that the previous assignments of configurations to some chlorocyclopropanes, obtained from additions of chlorocarbene to olefins, are in error.[3a] We have now synthesized the two adducts of chlorocarbene to 1-butene from *cis* and *trans* 1-chloro-1-butene *via* the Simmons-Smith reaction.[7] Identity of the product obtained from *trans*-1-chloro-1-butene with the minor adduct of the carbene reaction and *vice versa* established that here again the major product of chlorocarbene addition has the *cis* orientation and that the original assignments should be reversed.

A possible explanation of the observed stereochemistry may be found in the assumption of a transition state with considerable charge separation.[9] Partial delocalization of opposite charges over the alkyl groups by hyperconjugative effects and over the aryl and chlorine substituent, respectively, by inductive effects, will lead to smaller over-all charge separation in the *cis* transition state. Observed solvent dependence, leading to smaller ratios in more polar solvents, such as ether, concur with this explanation.[10] The striking similarity of the steric course of these carbene additions with the Diels-Alder reaction should be pointed out, and, perhaps, may be regarded to be more than just a coincidence.[11]

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[4] Determined according to C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[5] J. I. Musher, *ibid.*, **35**, 1159 (1961), and private communication.

[6] J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962), and references cited therein.

[7] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[8] The predominantly formed adducts of chlorocarbene to IV, V and VI show larger vicinal spin spin coupling and decreased shielding of the proton located on the carbon bearing the chlorine atom.[3a]

[9] This assumption is strongly supported by the established electrophilic nature of carbenoid intermediates: W. v. E. Doering and W. A. Henderson, *J. Am. Chem. Soc.* **80**, 5274 (1958); G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960).

[10] Naturally, other factors, such as the degree of bond formation in the transition state, determined in part by the ground state stability of the carbenoid intermediate will influence the magnitude of the isomer ratio as well. The small but experimentally significant preference for the formation of same isomer in the diazo compound photolysis indicates that the probable incorporation of a molecule of lithium halide in the transition state of the α-elimination reaction is not the sole factor in determining the stereochemistry.

[11] Satisfactory analyses have been obtained for all new compounds.

[12] A. P. Sloan Foundation Fellow, 1962-1964.

[13] National Science Foundation Predoctoral Coöperative Fellow, 1961-1963.

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RECEIVED SEPTEMBER 5, 1962

ON THE COPOLYMERIZATION OF BENZENE

Sir:

Considerable interest was generated by claims that benzene copolymerizes with vinyl acetate,[1] methyl methacrylate,[2] and styrene.[3] More recently, however, the vinyl acetate work has been refuted[4] and the styrene claim withdrawn.[5] Both sets of workers[4,5] found radioactive impurities in their benzene which led to erroneous results. Although the matter seems settled for these two monomers, the question of whether copolymeriza-

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[1] W. H. Stockmayer and L. H. Peebles, *J. Am. Chem. Soc.*, **75**, 2278 (1953); L. H. Peebles, Jr., J. T. Clarke and W. H. Stockmayer, *ibid.*, **82**, 4780 (1960).

[2] D. B. Anderson, G. M. Burnett and A. C. Gowan, IUPAC Symposium on Macromolecular Chemistry, Moscow, 1960, Sec. II, p. 111.

[3] G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **48**, 237 (1961).

[4] J. W. Breitenbach, G. Billek, G. Falthansl and E. Weber, *Monatsh. Chem.*, **92**, 1100 (1961).

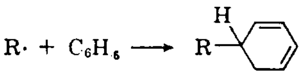
[5] G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **51**, 236 (1962).

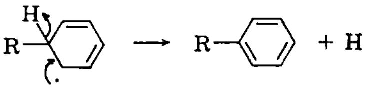
tion can take place with other monomers is still unanswered.

In an attempt to answer this question, we have studied the reactions of what is probably the most reactive polymer radical, the polyethylene growing chain. Ethylene was polymerized to low conversion in a batch reactor at 20,000 psi. and 130° using di-*t*-butyl peroxide initiator. Steady-state polymerization was demonstrated. Vapor chromatography of benzene-C^{14} as obtained disclosed the presence of a number of impurities. The pure benzene-C^{14} used in this study was obtained by trapping the benzene peak. Scintillation counting of the polymer made in the presence of this benzene-C^{14} indicated incorporation of a small but definite quantity of benzene in the polymer. Were this benzene to have been incorporated by chain-transfer with the growing polymer chains, a transfer constant of 9.7×10^{-4} would be calculated. From molecular weight measurements of polyethylenes prepared in the presence of large quantities of unlabeled benzene, a chain-transfer constant of $(9.4 \pm 0.8) \times 10^{-4}$ was obtained. Therefore, chain transfer, not copolymerization, takes place.

In order to give a significant answer to the main question, however, we must know why copolymerization failed in this instance. The reason for failure can be deduced from a knowledge of the mechanism for chain transfer. If transfer occurs *via* direct abstraction of hydrogen (scheme 1) then we can infer that copolymerization fails because the growing polymer chain does not add to benzene.

$$R\cdot + C_6H_6 \longrightarrow RH + C_6H_5\cdot \qquad (1)$$


(2a)


(2b)

However, if transfer occurs as suggested by Mayo[6] (scheme 2) we would conclude that copolymerization fails after addition of benzene takes place because the intermediate radical loses hydrogen more readily than it adds ethylene. More easily polymerized monomers might then be expected to copolymerize with benzene. Scheme (2) is plausible inasmuch as addition of methyl[7] and trifluoromethyl[8] radicals to benzene has been demonstrated.

In order to differentiate between the schemes, the chain-transfer constant of deuteriobenzene[9] was determined. The value obtained, $(5.6 \pm 1.1) \times 10^{-4}$, shows a strong isotope effect. If addition to a double bond of benzene (step 2a) were the rate-determining step, only a small isotope effect would be expected. Hence, 2a cannot be the rate determining step. Step 2b should show a large isotope effect. However, for it to be rate-determining, either the polymerization rate would have to be reduced seriously or step 2a would have to be readily reversible. Deuteriobenzene would retard the rate more than benzene. It is our experience that reactions similar to 2a are not reversible. Furthermore, only a slight rate reduction was observed and deuteriobenzene retarded the rate less than benzene. Therefore, scheme 2 cannot be the mechanism of transfer and scheme 1, which fits all the evidence, must be correct. Copolymerization fails because addition to a double bond of benzene does not take place.

In conclusion, we have found that even the highly reactive primary alkyl radical, a growing polyethylene chain, does not add to benzene. When polyethylene chains react with benzene it is by direct abstraction of hydrogen. We therefore believe that free-radical copolymerization of benzene is impossible.

We acknowledge the helpful discussions of Mr. Eli Perry.

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TEXAS CITY, TEXAS LLOYD C. ARNOLD

RECEIVED OCTOBER 25, 1962

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[6] F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).

[7] M. Levy, M. Steinberg and M. Szwarc, *ibid.*, **76**, 3439 (1954).

[8] J. L. Holmes and K. O. Kutschke, *Trans. Faraday Soc.*, **58**, 333 (1962).

[9] Supplied through the courtesy of Monsanto Research Corporation which obtained it from Ciba, Switzerland. Mass spectrographic analysis indicated 99.9% C_6D_6.

A NON-CARBENOID RING EXPANSION OF A BENZENOID SYSTEM

Sir:

We wish to report a remarkable one-step ring expansion of a benzenoid system (phenoxide ion) by a species other than a carbenoid entity (chloramine). Although the ambident character of phenoxide ions has been clearly demonstrated in the classical studies of Claisen,[1] Curtin,[2] Kornblum[3] and their associates, attention has been directed only to alkyl, alkenyl and aralkyl halides as alkylating agents.[4] It seemed apparent that the synthetic applicability of this method could be generalized and we were led to investigate the reaction of the sodium salts of 2,6-disubstituted phenols with chloramine. This procedure does not lead to the simple O-arylhydroxylamines,[5] but instead results in the ring enlargement of the phenoxide moiety to give 1,3-dihydro-2H-azepin-2-ones (I) and thus provides a facile synthetic entry into this

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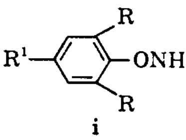
[1] L. Claisen, F. Kremers, F. Roth and E. Tietze, *Ann.*, **442**, 210 (1925); L. Claisen, *Z. angew. Chem.*, **36**, 478 (1923).

[2] D. Y. Curtin and D. H. Dybvig, *J. Am. Chem. Soc.*, **82**, 225 (1962), and leading references contained therein.

[3] N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

[4] A study of the action of sodium 2,6-dimethylphenoxide on perchloryl fluoride has been reported recently; *cf.* A. S. Kende and P. MacGregor, *ibid.*, **83**, 4197 (1961).

[5] The interaction of phenoxide ions with chloramine has been previously described: (a) W. Theilacker and E. Wegner, *Angew. Chem.*, **72**, 131 (1960); (b) W. Theilacker, *ibid.*, **72**, 498 (1960). Although a direct comparison of samples has not been made, these workers appear to have formulated the reaction products incorrectly as O-arylhydroxylamines (i):


i